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Molecular Spectroscopy at Corrugated Metal Surfaces

by

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Spectroscopic properties for molecules in the vicinity of metal surfaces are usually determined by the energy-transfer mechanisms between the admolecules and the substrate, which can involve various collective excitations of the substrate electrons such as surface plasmons and excitons. A brief review of this subject, including various phenomena such as fluorescence and photoabsorption lineshapes, is presented. The review includes recent work of the authors, with emphasis on the effects due to surface corrugations. Examples which illustrate possible applications of such studies in the areas of surface photochemistry and heterogeneous catalysis are also discussed.

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Molecular Spectroscopy at Corrugated Metal Surfaces

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ABSTRACT

Spectroscopic properties for molecules in the vicinity of metal surfaces are usually determined by the energy-transfer mechanisms between the admolecules and the substrate, which can involve various collective excitations of the substrate electrons such as surface plasmons and excitons. A brief review of this subject, including various phenomena such as fluorescence and photoabsorption lineshapes, is presented. The review includes recent work of the authors, with emphasis on the effects due to surface corrugations. Examples which illustrate possible applications of such studies in the areas of surface photochemistry and heterogeneous catalysis are also discussed.

Since the work of Purcell (1) which dates back to the 1940's, it has been known that the spectroscopy of a gaseous system can be dramatically influenced by its environment. In particular, molecular spectroscopy for systems located in the vicinity of a surface has received considerable attention during the past twenty years. Spectroscopic observables such as photoabsorption cross sections, lineshapes, and other fluorescence observables such as line broadenings and level shifts in the presence of a substrate surface, are typically quantities of most interest. Motiviations that lead to such intensive studies are various. On the pure academic side, it is of interest to understand the various interactions between the adsorbates and the substrate surface, which presents a complicated problem since it is a many-body system that does not possess bulk symmetries. On the practical side, it is expected that such study will lead to applications in areas ranging from surface photochemistry to material structures and propeties of the substrate surface. In the former area, for example, if one assumes the properties of the substrate surface is well understood (through other studies such as LEED analysis), one can then study the photoabsorption cross section of admolecules which can yield useful information in regard to the ultimate goal of laser-assisted heterogeneous catalysis (2). On the other hand, if one supposes that the spectroscopic properties of admolecules to be well understood, one can then use such knowledge as a probe for the electronic (and lattice) structure and properties of the substrate surface.

In this article, we shall discuss spectroscopic propeties of molecules at corrugated metal surfaces. The role of surface roughness has been recognized to be prominent in various surface processes since the discovery of the surface-enhanced Raman effect in 1974 (3). Since there is a comprehensive review on surface spectroscopy covering work prior to 1984

(4), here we shall review progress, with emphasis on our own work, made in just the past several years. We shall pay particular attention to fluorescence of the admolecules, where the case for a perfectly flat surface has already been discussed extensively (5). We shall also review briefly some phenomena concerning photoabsorption and lineshape. Finally, we shall mention some possible applications in photochemistry at surfaces.

FLUORESCENCE

This kind of study is usually carried out using an experimental setup of the "sandwich-type" as shown in Fig. 1. A layer of fluorescent molecules is separated from the substrate surface by a spacer which controls the molecule-surface distance (d). An incident laser pulse of width shorter than the lifetimes of the admolecules excites the molecules, and the deexcitation emission intensities are analyzed by various time-resolved techniques (standard raw data are reproduced in Fig. 2). For a fixed fluorescence/phosphorescence emission frequency (ω), the decay rates (γ) for the admolecules can then be studied as a function of d; or likewise, one can fix d and study γ as a function of ω, which will be more involved in the excitation process in the experiment. At distances very close to the surface where γ is very large, phosphorescent molecules will be preferred; otherwise, one would require a laser pulse of extremely narrow width and very fine time-resolved equipment.

The simplest theoretical description for this kind of experiment is the classical phenomenological (CP) approach in which the admolecule is modeled as a point dipole satisfying the equation of motion for a damped harmonic oscillator driven by the surface field ($\vec{E}_s$). This leads to the level shift and the induced decay rate of the form

$$\Delta\omega = \frac{\gamma^2}{8\omega_0} + \frac{\alpha}{2\omega_0} \, \text{ReG} \quad , \quad \gamma = \gamma_0 + \frac{\alpha}{\omega_0} \, \text{ImG} \quad ,$$

where ω_0 and γ_0 are the free-molecule level spacing and linewidth, respectiely, α is an electromagnetic coupling constant, and the dyadic function G ($\equiv \text{\tiny{S}}_s/\mu$) is defined as the surface field acted on the molecule per unit dipole moment (μ). Since $\gamma_0 \ll \omega_0$ in general, it is not difficult to see that $\Delta\omega$ may often be neglected compared to the surface effect on γ. The remaining task is then to calculate the function G.

In general, there are two ways of calculating E_s within the CP aproach. The more exact treatment involves solving the exact electrodynamics of the dipole-surface system (where E_s is given by the reflected field at the dipole site); this is known as the energy transfer theory (ET) since the result for the total rate γ can be separated clearly in terms of the contribution from the radiative and nonradiative transfers. In another, cruder description, one would consider the "static limit" of the problem and replace the effects due to the surface by the image dipole, whereby E_s is simply given by the image field. For the case of a flat surface, this image theory (IT) simply leads to the "inverse cube rule" for the variation of γ versus d, and the "oscillation behavior" at far distances is well explained by the exact theory (ET) established by Chance, Prock and Silbey (CPS) (5) through the application of Sommerfeld's theory for a radiating antenna above the surface of the earth (6). This CPS theory has been successful in explaining the experimental data of Drexhage and coworkers (7) as illustrated by the example reproduced in Fig. 3, where the fluorescence of the Eu^{+3} complex has been studied using fatty acids as the spacer.

For the case of a rough surface, however, the fluorescence problem has been previously limited to the IT approach due to the mathematical complications for the dynamics of the problem (8). It has been a wide belief that as long as $d \ll \lambda$, where λ is the emission wavelength (e.g., $d \sim 10^2$ Å in the region for the most pronounced surface morphological effects and $\lambda \sim 10^3$ Å for fluoresence in the visible range), IT should be accurate enough for the description of the phenomenon (8). However, in a recent analysis (9), it has been found that the condition $d \ll \lambda$ is not sufficient and IT can break down appreciably for a highly-conducting substrate such as a noble metal. The physical reason for this stems from the fact that the dynamic Helmhotz wave equation in a metal __does__ __not__ reduce to the static Poisson equation in the long-wavelength limit if the conductivity of the metal becomes very large. Hence, we conclude that it is always desirable to rely on ET for any dipole-surface problem, be it a flat or a rough surface.

The motivation for studying the decay rates at rough surfaces comes from some recent experiments. Looking at Fig. 3 carefully, we see that the CPS theory fits the experiment very well in the large distance regime ($d \sim 10^3$ Å). However, this simple CP approach is expected to fail for very close distances, since the surface cannot be regarded as an abruptly discontinuous boundary due to the "quantum spreads" of the surface electrons. Nevertheless, it has been established that as long as $d \geq 10$ Å, such microscopic effects can be ignored and the CP approach should be valid (10). On the other hand, in a recent experiment carried out by Harris and coworkers (11), in which the phosphorescence of biacetyl ($^3n\pi*$) was studied above a silver surface using liquid ammonia as the spacer for distances in the range between 20 and 100 Å, discrepancies were observed between the CPS theory and the data. The theory was found to lie either above or below the

best fit to the data. These researchers tried to explain the discrepancies by resorting to a surface-damping model of Persson and Lang (12) based on the electron-hole pair excitation mechanism. While this is a possible justification, we would like to consider other alternative possibilities such as the effect of surface roughness at such close distances. As a matter of fact, some time even earlier, a group at Bell Laboratories carried out a similar type experiment of triplet pyrazine on silver with liquid argon as the spacer, where discrepancies between the CPS theory and the data were observed with the data lying above the theory (13). While these researchers blamed the inaccuracy in the dielectric constants they used to compute the CPS theory, we suspect that roughness may have again played a role in their experiment. In fact, in an even earlier experiment, the same researchers had reported with the help of a scanning electron microscope the observation of an almost periodic structure because of the surface finish of the underlying sapphire due to the polishing (14). All of these observations led us recently to carry out theoretical studies on the effects of surface roughness on admolecular decay rates, which we shall now describe briefly.

For the case where the roughness is shallow, we have established a dynamic theory (ET) for the admolecular decay rates adopting a perturbative approach (15). Essentially, we have solved the Sommerfeld problem (6) for a "rough earth". In particular, we have considered the simplest kind of surface morphology, namely, a shallow sinusoidal grating, where we have combined the CPS theory (5) with the theory published by Maradudin and Mills (16) for light-scattering phenomena employing the Green's function technique. Figure 4 reproduces some of our results in which we have plotted the ratio $R \equiv \gamma^R / \gamma^F$ versus d with γ^R being the induced decay rate for the

case of a silver grating surface and γ^F the flat surface value from the CPS theory. The curves a, b, c and d correspond to different emission frequencies and different grating parameters. Let us make the following three observations: (i) as one goes farther from the surface, the effect of the surface roughness disappears ($\mathcal{R} \rightarrow 1$) as expected; (ii) the CP approach breaks down explicitly at very close distances (note that the curve 4(d) dips below zero!), so that we conclude our numerical results to be trustworthy only for d beyond, say, about 10 Å; and most importantly, (iii) depending on the various parameters, the roughness can enhance or diminish the flat surface value, in qualitative agreement with the experimental observations we describe above.

For the case of large roughness, it becomes impractical to carry perturbation theory to higher orders. Here one can introduce the so-called "island-surface" model as depicted in Fig. 5. Instead of looking at the actual profile of the surface, we model it as a collection of "islands" (bumps) of unlimited sizes. The simplest kind of bump is a sphere. The decay rate problem of a dipole near a collection of spheres has been worked out by Liver, Nitzan and Freed using the IT approach (17), and the problem for "a single island" (an isolated sphere) has been worked out using the dynamic ET approach (18). We are presently in the process of constructing an ET approach for a realistic island surface by generalizing our previous work to include the effects of the neighboring spheres. Until this is done, we believe that a fully-dynamic description of the decay problem for very rough surfaces is still unavailable for the comparison with experimental results.

So far, we have been focussing on the molecule-surface distance (d) behavior of the induced decay rates for molecules at a rough surface. We

have also looked into the decay rate spectrum as a function of the emission frequency at a fixed d. We have observed, aside from the ordinary surface-plasmon (SP) peak, an extra resonance structure induced by the presence of roughness which is morphology-dependent. Furthermore, this extra peak is predicted only from ET but not from IT. Figure 6 shows the comparison of the two theories at a very close distance (50 Å) for a silver grating surface (19), where IT is expected to be very accurate. We observe that for cases where the grating wave number (Q) is close to the emission wave numbers (k) such as in curves 6(b) and 6(c), ET predicts a resonance at an emission frequency with k $\approx$ Q. The position of this new peak moves as Q varies and grows as the amplitude of the grating is increased. One can imagine that this morphology-dependent peak may move and grow to overshadow the ordinary SP peak, so that in actual experiments one observes a kind of "peak shift" in the spectrum. Previously, there has been a controversy as to whether surface roughness causes "peak shifts" in the energy-loss spectrum obtained from an electron scattering experiment with a Mo surface (20). Our results obtained for the decay-rate spectrum shed some light on the above issue. This morphology-induced resonance peak should be a very general phenomenon and should show up for any kind of rough surfaces. Recently, we have repeated such a decay-rate spectrum study for a spherical surface in an attempt to understand the physical origin of this new peak (21). Figure 7 shows one of our calculations where we have split the total decay rate into radiative and nonradiative components, respectively. It is obvious that the roughness-induced peak has its origin in radiative transfer from the molecule in the presence of the surface. The same origin should be responsible for the peak which appears for the grating surface. Moreover,

nothing happens in case of a flat surface since the surface plasmon modes can couple to radiative modes only in the presence of surface roughness.

To wind up our discussion on fluorescnece phenomena, let us consider another substrate system of great interest, namely, a corrugated thin film. When there are two rough surfaces which can each support a SP mode, an interesting phenomenon known as "cross coupling" can occur when the two SP's are excited resonantly at the same time. This in turn can lead to dramatic effects such as SP-induced transparency in a metal film (22). This can have technological applications in device designs since one can then "plate" a dielectric substance (e.g., polymer) so that it becomes electrical conducting but without becoming opaque. While it has been controversial as to whether such cross-coupling phenomenon has indeed been observed in various light-scattering experiments (23), recently a group at the University of Rochester has claimed on unambiguous observation of this phenomenon through molecular fluorescence studies on a thin grating silver film (24). We are at present trying to generalize our previous theory for a single grating surface (15) to such a system in order to better understand the experiment.

PHOTOABSORPTION LINESHAPE

Aside from fluorescence studies, investigations into the photoabsorption rates and spectral lineshapes can also yield useful information concerning admolecules and the substrate surface. Experimentally, instead of using a laser pulse to excite the admolecules, here one would illuminate the adlayer by a CW laser and analyze the absorption spectrum. This has been reviewed elsewhere (25) and here we shall only give a brief sketch of the subject. The two main concerns here

are (i) the enhancement ratio (r) in the photoabsorption/dissociation process, which is defined as the ratio between the absorption cross sections with and without the presence of the surface, and (ii) the distortions in the lineshape $I(\omega)$ of the spectrum due to surface effects. There is extensive literature on this subject covering all sorts of molecular spectra such as vibrational (26), rovibrational (27) and electronic (28) spectra for both physisorbed (26-28) and chemisorbed (29) molecules. Furthermore, different kinds of surface morphologies have also been considered ranging from the shallow grating model to a sphere-modeled "island surface" (28). Due to the surface-damping effect as discussed in the previous section, which will now compete with the surface enhanced field, one can then introduce the concepts of a critical molecule-surface distance (below which $r < 1$) and an optical distance (at which r is maximum) to describe the photoabsorption/dissociation phenomenon (25). Furthermore, by looking at the distortions of $I(\omega)$, one can learn about the response of the substrate surface to that particular molecular process. As an example, the "double-. peak feature" and the "sharp-edge window" which appear in the distortions of a free molecular absorption (Lorentzian) profile in the presence of a spherical or shallow-grating surface signify the effects of the surface plasmon on the photoabsorption process (28). Even for a flat surface, an interesting phenomenon noticed by Langreth (30) is that the original (free) molecular lineshape cannot remain Lorentzian, but is distorted towards a Fano-type profile, if electron-hole pairs are created in the substrate due to energy transfer from the excited admolecule. Moreover, most previous studies have assumed the free-molecule profile $I_0(\omega)$ to be symmetric (often Lorentzian), so that asymmetric distortions are brought about by the presence of the surface. Recently, we have also initiated a

phenomenological study of the case where $I_0(\omega)$ is already asymmetric in nature (31). *Some preliminary results for a shallow-grating surface have* been obtained for $I_0(\omega)$, having the form of a Fano profile in which the double-peak feature again appears with the broadening of the original profile window at the steep edge near the low-frequency end, and the creation of a new window at the high-frequency end due to the surface plasmon resonance is observed (see Fig. 8). This study should shed some light on processes like autoionization and predissociation for molecular systems in the vicinity of a surface. We hope that more rigorous studies will be carried out in the future.

CONCLUSIONS

In the above, we have discussed various issues concerning molecular spectrosocpy at corrugated metal surfaces, paying particular attention to our own work developed in the past two years. We feel that the most interesting issue which still awaits for experimental confirmation is whether roughness should always enhance the flat-surface values for the induced decay rates, or as we have shown, both enhancement and diminution can occur. This may find practical relevance in laser-assisted heterogeneous catalysis where one wants to maximize the photoabsorption rate of the reagents through the enhanced surface fields so that the molecules can be dissociated efficiently to undergo various reactions. In this case, it is well known that the surface-induced line-broadening effect will tend to suppress the absorption rate, thus lowering the photochemical yield. However, according to our findings, one can make use of the surface roughness to suppress such line broadenings by carefully controlling the various factors involved in the process. Hence, an experimental

clarification of this issue is of prime importance. Another interesting feature we have found is the roughness-induced peak in the decay rate spectrum which still awaits for experimental verifications, although similar effects have been observed in light-scattering experiments (32). Finally, we want to emphasize that fluorescence.and other spectroscopic studies for admolecular systems can lead to a deeper understanding of the substrate surface as well as possible surface-induced chemical processes that can take place in the vicinity of the surface.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

1. Experimental setup for studying molecular fluorescence at a surface.

2. Samples of standard raw data for fluorescence at a surface for various molecule-surface distances. The data are taken from the phosphorescence study of triplet pyrazine on silver surface and are reproduced as in Fig. 1 of Ref. 13.

3. Example showing the success of the CPS theory for a double-mirror system, as reproduced from Fig. 6 of Ref. 5(b).

4. Ratio ($\mathcal{R}$) of the decay rates for a silver grating surface to that for a flat surface as a function of the molecule-surface distance for various emission frequencies (ω) and grating wave numbers (Q). Curve a: $\omega = 2 \times 10^4$ cm^{-1}, $Q = 0.08$ Å^{-1}; curve b: $\omega = 2 \times 10^4$ cm^{-1}, $Q = 0.01$ Å^{-1}; curve c: $\omega = 3 \times 10^4$ cm^{-1}, $Q = 0.01$ Å^{-1}. Curve d — $\omega = 3 \times 10^4$ cm^{-1}, $Q = 0.08$ Å^{-1}. The grating amplitude ς_0 is fixed at 0.7 Å.

5. The "island-surface model" for the molecular fluorescence problem at a surface with large corrugations.

6. Decay-rate spectrum for a molecule located at $d = 50$ Å above a silver grating surface of varying roughness parameters (ς_0,Q). Curve a: $\varsigma_0 = 1$ Å, $Q = 1 \times 10^{-2}$ Å^{-1}; curve b: $\varsigma_0 = 1$ Å, $Q = 1 \times 10^{-3}$ Å^{-1}; curve c: $\varsigma_0 = 10$ Å, $Q = 1.25 \times 10^{-3}$Å^{-1}. The solid line represents the results from ET and the dotted line results from IT.

7. Decay-rate spectrum for a molecule located at d = 700 Å from the center of a silver sphere of radius a = 500 Å according to ET. The solid, dotted and dashed curves denote the total, radiative and nonradiative rates, respectively.

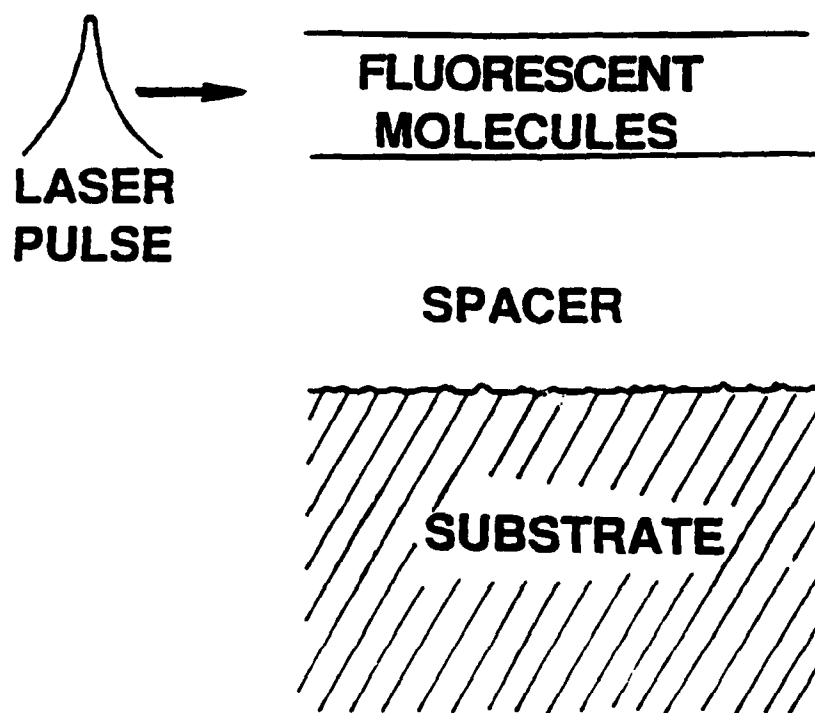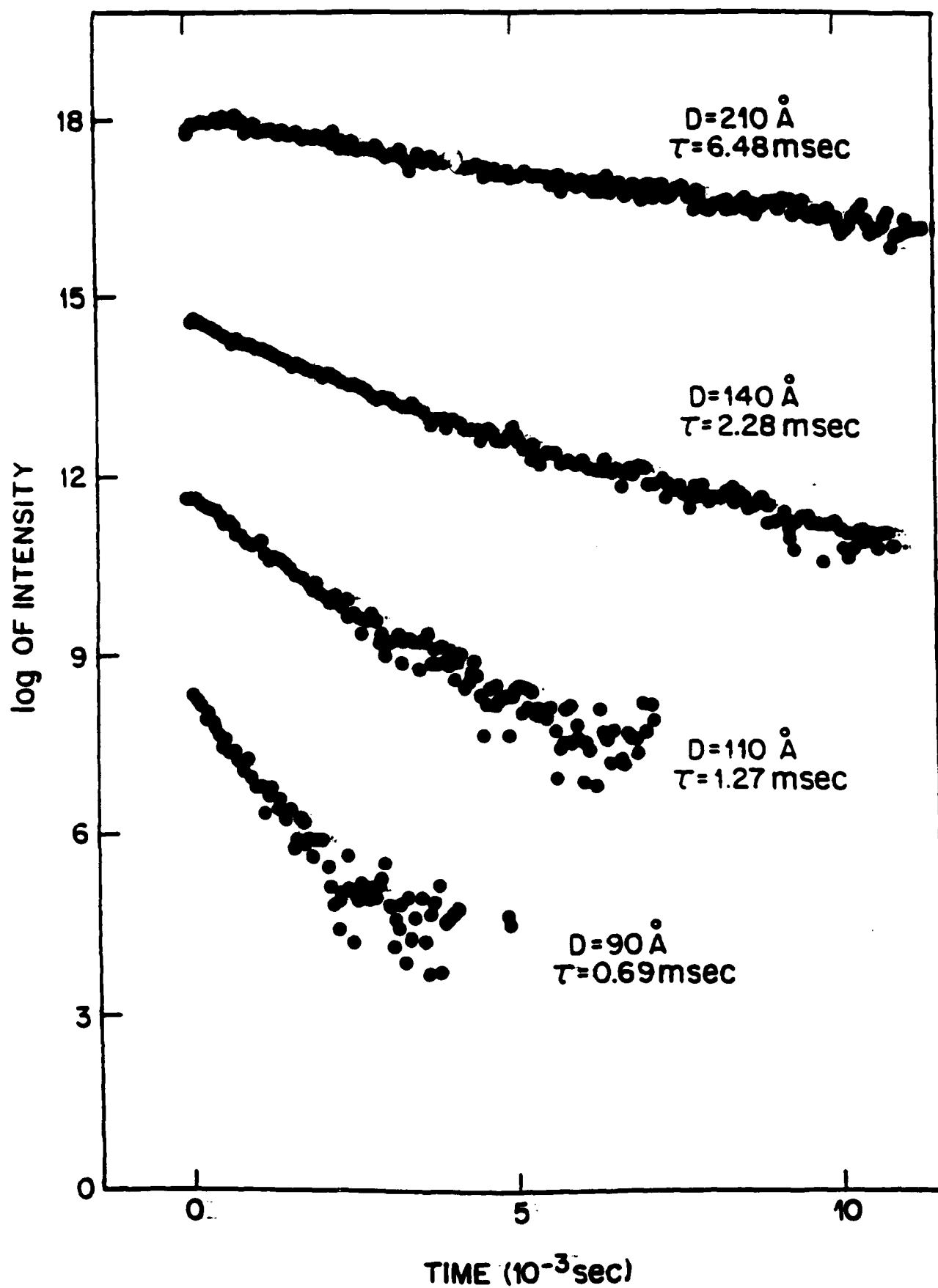8. Distortion of the Fano profile $I_0(\omega)$ which simulates certain molecular predissociation processes at a silver grating surface. The y-axis is in arbitrary units.
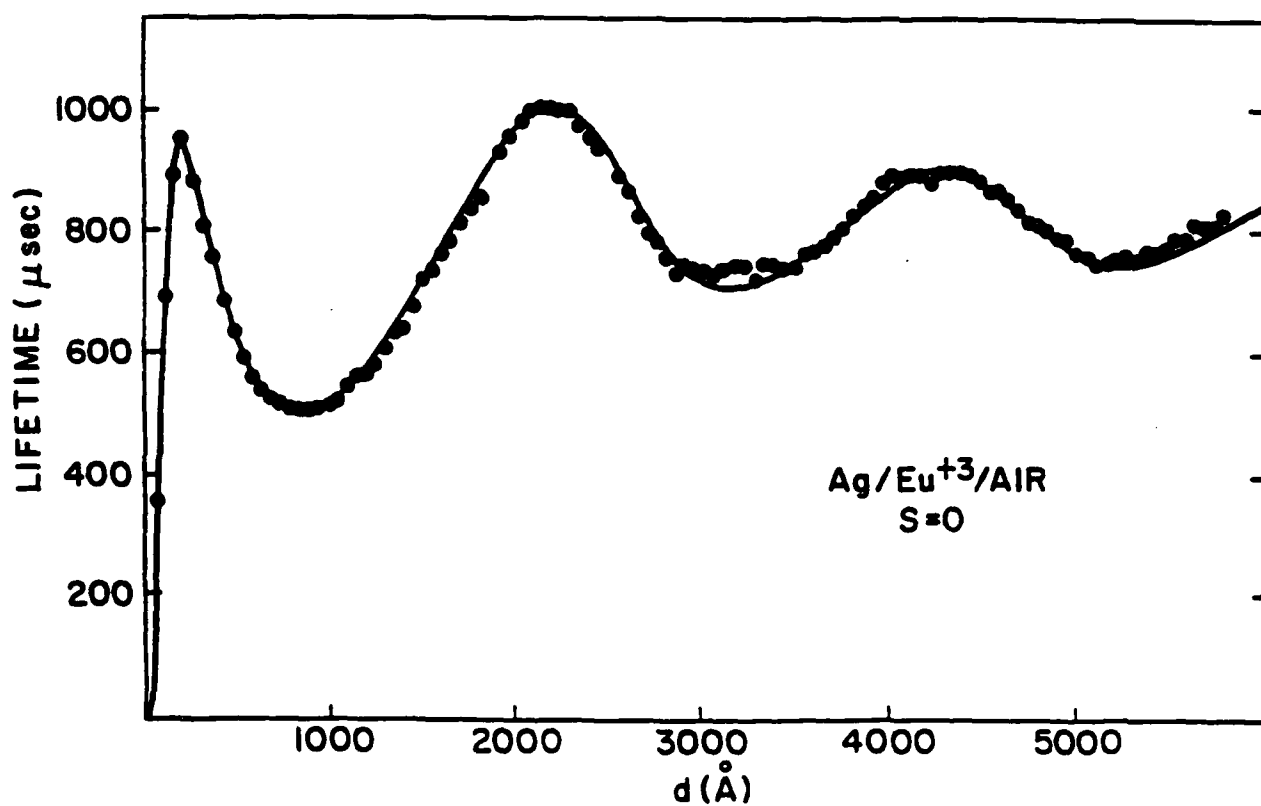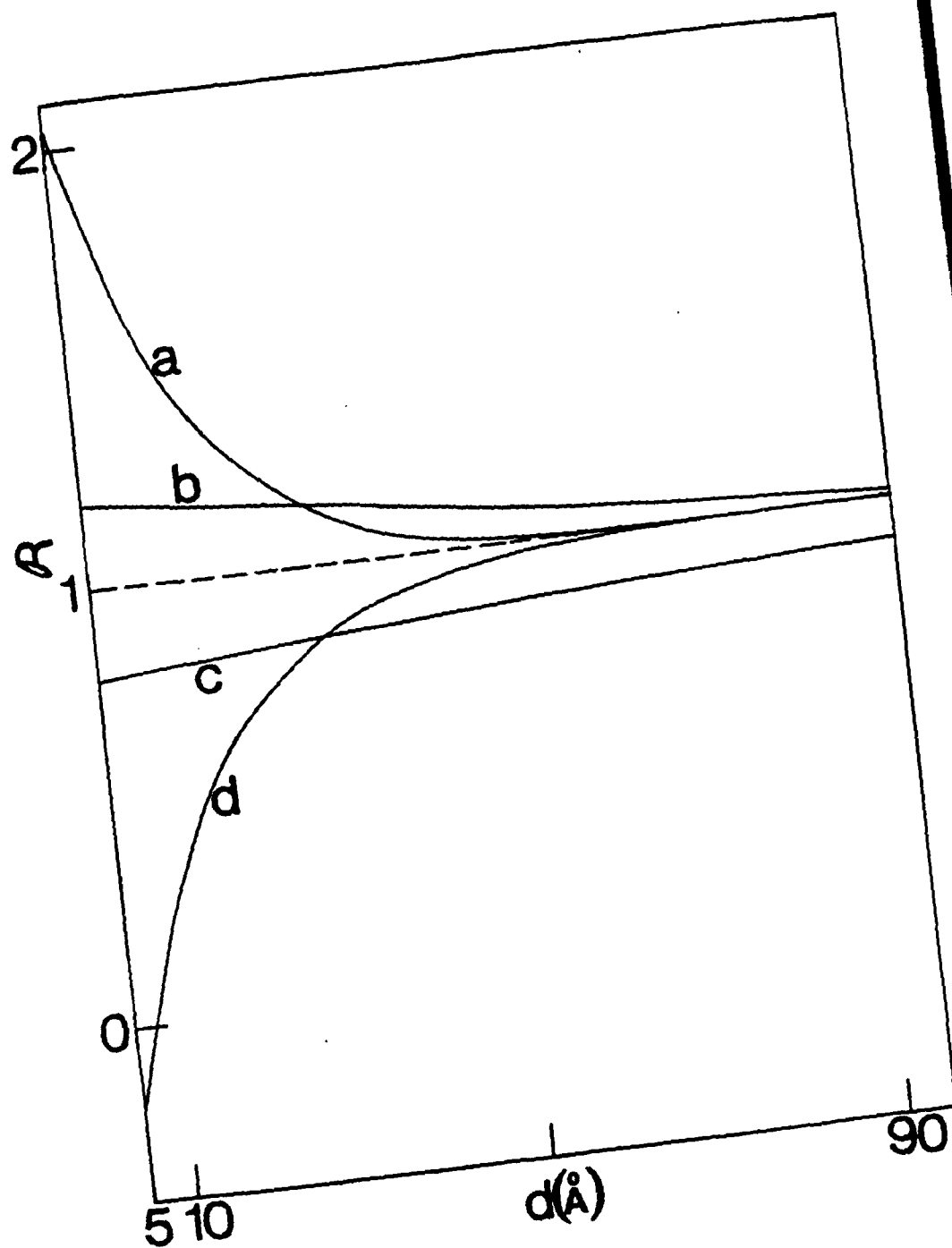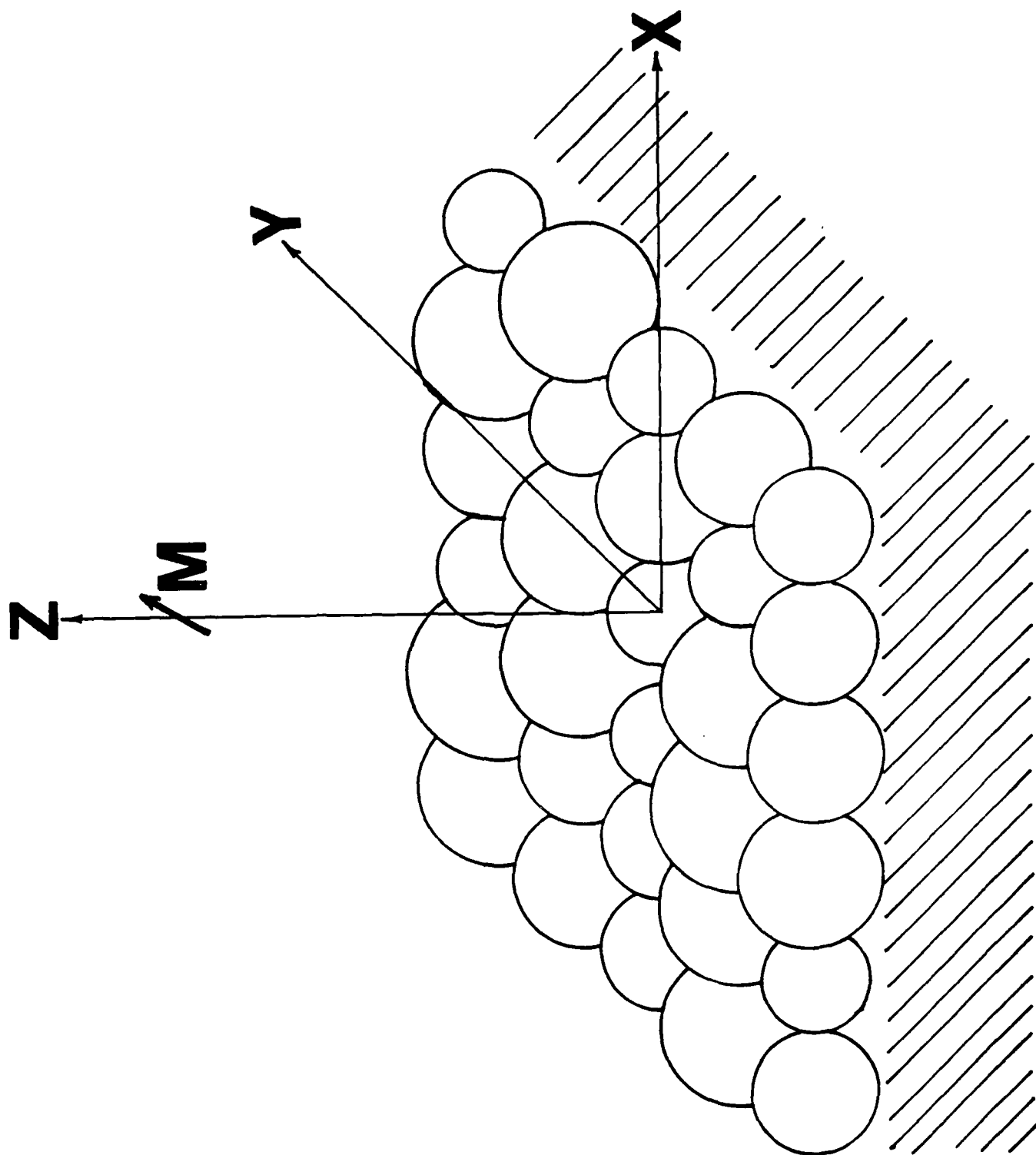
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6
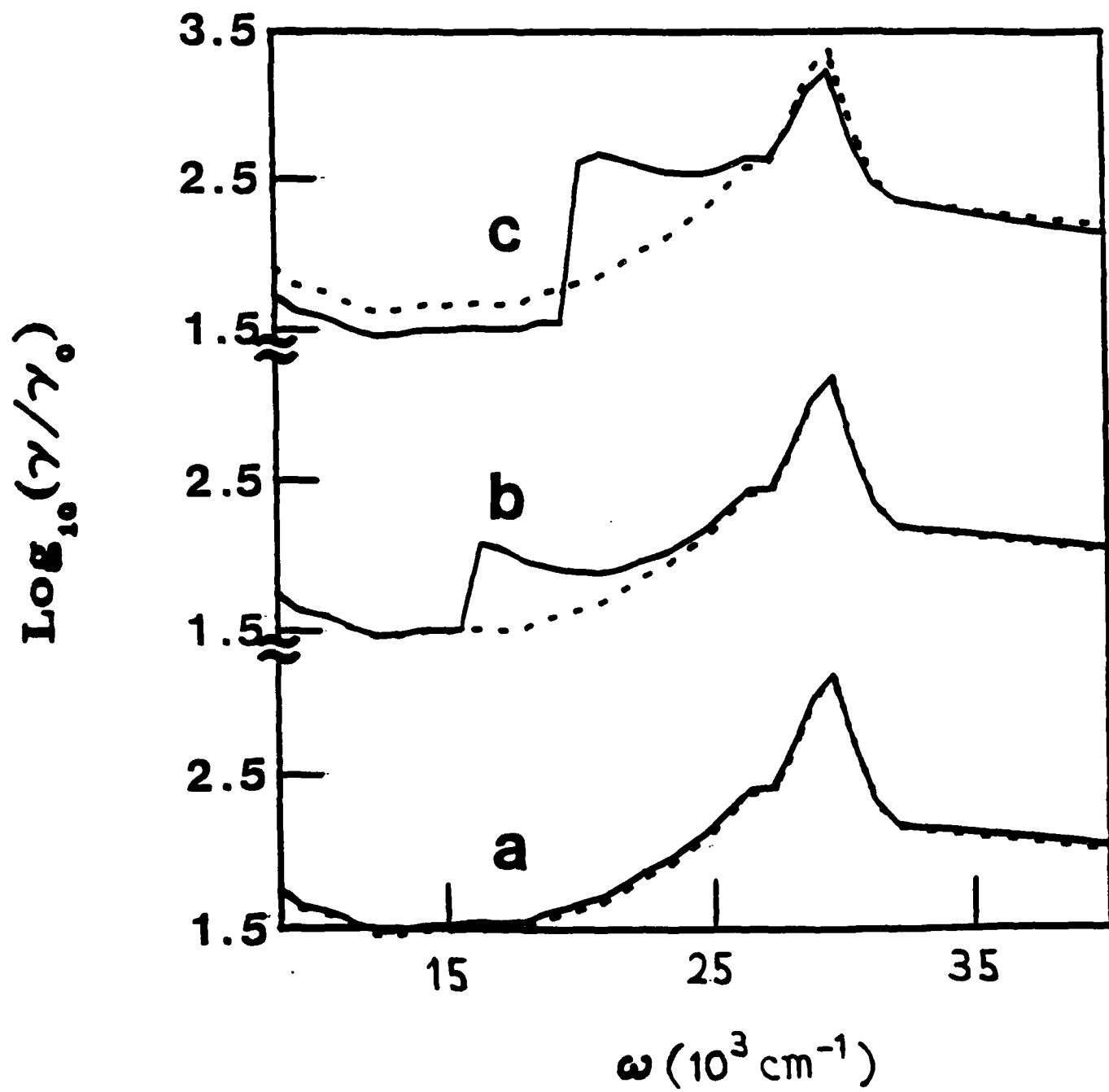
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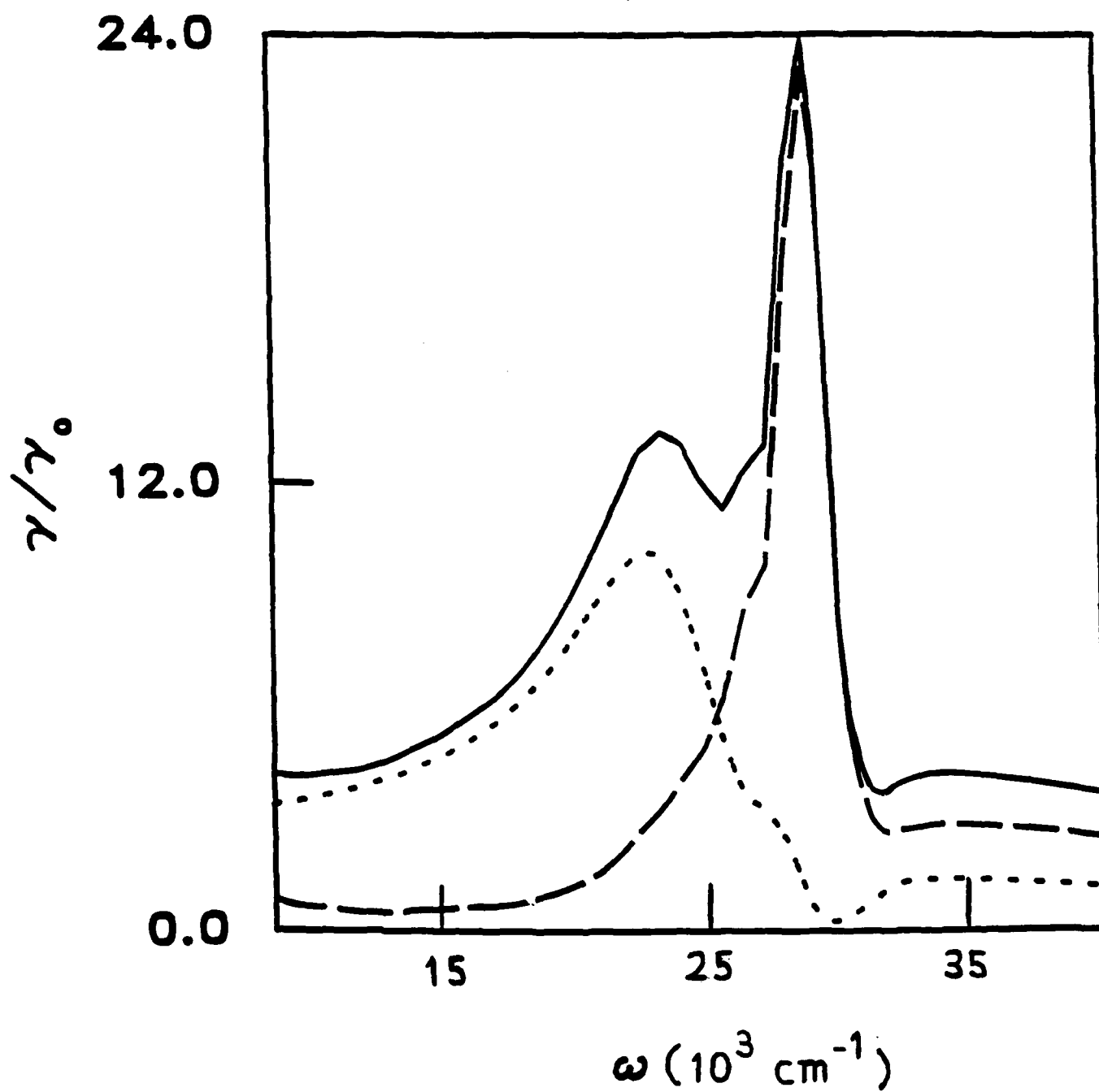
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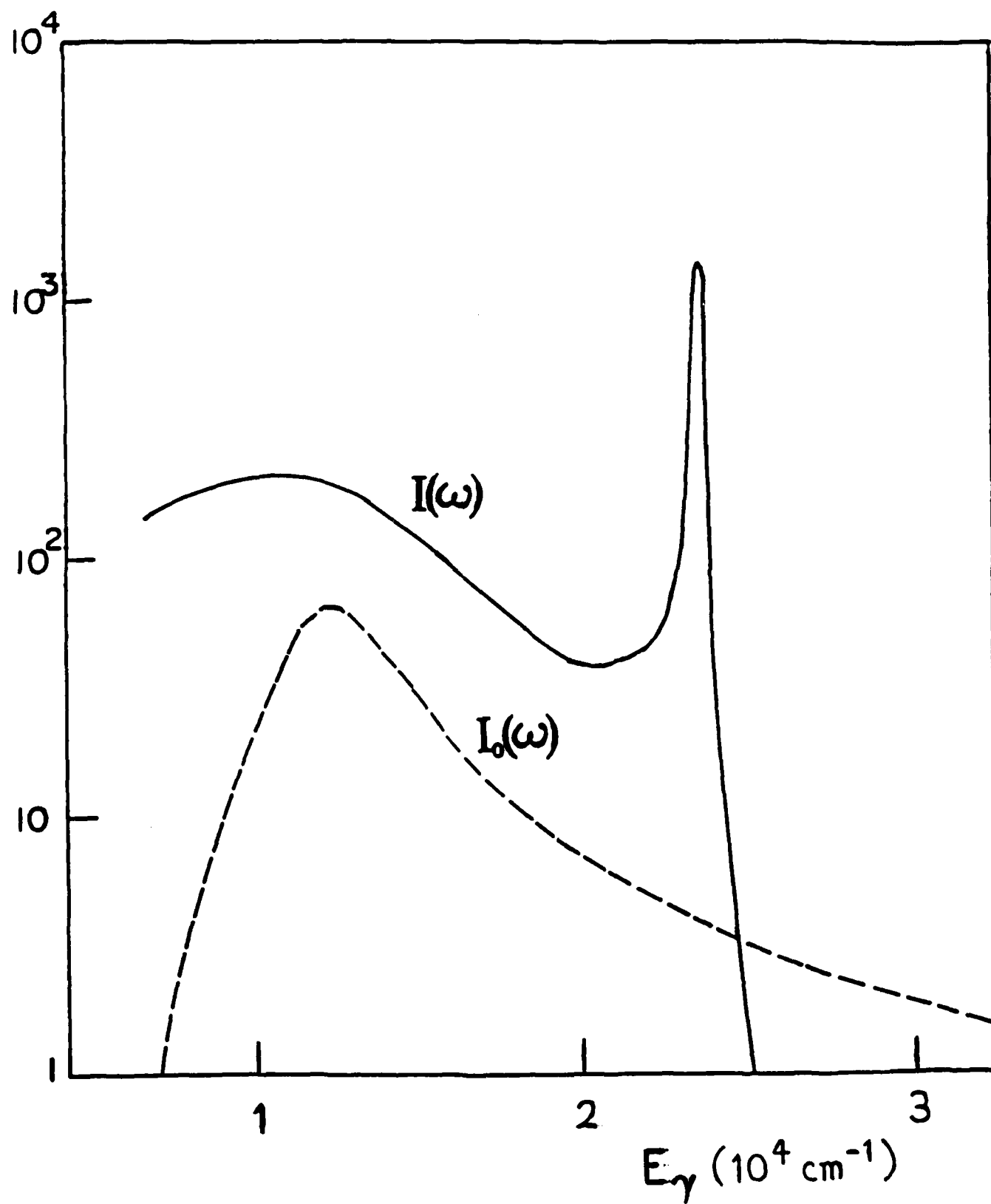
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